In search of extant Tc in the early solar system: ^{98}Ru and ^{99}Ru abundances in iron meteorites and chondrites

Harry Becker*, Richard J. Walker

Isotope Geochemistry Laboratory, Department of Geology, University of Maryland, College Park, MD 20742 4211, USA

Abstract

The short-lived ^{98}Tc–^{98}Ru (Half-life between 4 and ∼ 10 Ma) and ^{99}Tc–^{99}Ru (Half-life 0.21 Ma) decay systems have the potential to provide important information on the relative chronology of processes that affected metal phases in the early solar system. The proof of extant ^{99}Tc in the solar system would also tightly constrain the time interval between production of the nuclide and injection of *s*-process isotopes into the protosolar cloud.

High-precision Ru isotopic data for group IIAB (Negrillos, Bennett County, Coahuila, Filomena, Old Woman) and IIIAB (Casas Grandes, Costilla Peak) iron meteorites, and the chondrites Allende (CV3) and Allegan (H5) indicate that the isotopic compositions of ^{98}Ru and ^{99}Ru in these meteorites overlap with the terrestrial values at the ± 0.8 and ± 0.3ε levels (parts in 10,000), respectively. Previous reports of positive deviations of ^{98}Ru in Negrillos and Casas Grandes likely reflect inaccurate measurements.

Evaluation of processes that may fractionate Tc/Ru in solar system objects suggests that this ratio likely varied by only a factor of 2 or less. Using this constraint and solar system initial abundances of ^{99}Tc derived from astrophysical models, evolution models for the ^{99}Tc–^{99}Ru system predict deviations in ^{99}Ru of >0.3ε only, if these fractionation events occurred during collapse of the molecular cloud (< 10 ka). Thus, positive identification of enriched ^{99}Ru may require better than 0.1ε unit resolution. Absence of resolvable ^{98}Ru deviations indicates ^{98}Tc/^{96}Ru$_{\odot i}$ < 2 × 10^{-5}.
© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Technetium; Ruthenium isotopes; Solar system; Iron meteorites; Chondrites

1. Introduction

The Tc–Ru isotopic chronometers have received only limited attention as potential tools for early solar system chronology (Poths et al., 1987; Yin, 1995; Smoliar, 1998). ^{98}Tc decays to ^{98}Ru via the β$^-$ transition. Its half-life is poorly constrained to somewhere between 4.2 and 10 Ma (Kobayashi et al., 1993; Firestone and Shirley, 1996). The half-life of ^{99}Tc, which decays via the β$^-$ transition to ^{99}Ru, is only 0.21 Ma (Firestone and Shirley, 1996). Technetium has neither stable, nor, from a geological point of view, long-lived radioactive isotopes. Its chemical properties in near-surface aqueous environments are similar to those of Re (Greenwood and Earnshaw, 1994). The properties of metallic Tc under reducing conditions and at high temperatures and pressures are poorly constrained, and were only recently evaluated by experiments (Lazar, 2001).

* Corresponding author. Tel.: +1-301-405-4088; fax: +1-301-314-9661.

E-mail address: hbecker@geol.umd.edu (H. Becker).

Both Tc and Ru are refractory, highly siderophile elements (HSE). This means that most of their mass condensed at high temperatures in the condensation sequence from hot solar gas (Palme and Wlotzka, 1976), and that they have very high metal–silicate partition coefficients during core segregation (O'Neill et al., 1995). Processes that might have fractionated these elements in the early solar system include condensation and evaporation of dust grains, metal–silicate segregation, core crystallization, and aqueous alteration.

The relevance of a study of the Tc–Ru systems lies in potentially new constraints on the history of refractory metal phases in the early solar system. The short half-life of ^{99}Tc requires that any enrichment of ^{99}Ru in early solar system objects would have been the consequence of very early Tc–Ru fractionation, most likely resulting from high-temperature condensation or evaporation processes. Because of the short half-life of ^{99}Tc such results could yield constraints on the decay interval between the formation of s-process nuclides and incorporation into condensates in the solar nebula (e.g., Wasserburg, 1985). The ^{98}Tc–^{98}Ru decay system, with the longer half-life, may yield important information about the chronology of core segregation or the crystallization of solid asteroidal cores. Such data could lead to precise constraints on the relative time scales of these processes, complementing existing data from long-lived decay systems such as ^{187}Re–^{187}Os and ^{190}Pt–^{186}Os, and short-lived decay systems such as ^{107}Pd–^{107}Ag and ^{182}Hf–^{182}W.

Early Ru isotopic studies of iron meteorites showed no deviations from terrestrial values (Feitknecht et al., 1962; Herr et al., 1958). However, the analytical precision of these data was modest in comparison to current capabilities. ^{98}Ru is difficult to measure precisely, because it is a minor isotope (1.88 at.%) with the additional disadvantage of the existence of the abundant ^{98}Mo isobar (24.2 at.%). In contrast, ^{99}Ru is abundant (12.7 at.%) and there are no known isobars present when analyzed by thermal ionization mass spectrometry (TIMS). Ruthenium isotopic data on calcium–aluminum-rich inclusions (CAIs) from the carbonaceous chondrites Allende and Leoville were obtained by Poths et al. (1987), using a positive TIMS (P-TIMS) technique. This work showed that the abundances of ^{98}Ru and ^{99}Ru in the inclusions are indis-

tinguishable from a terrestrial Ru standard at the $\pm 10\varepsilon$ and $\pm 2.6\varepsilon$ ($\varepsilon =$ parts per 10,000) level (2σ), respectively. An in situ ion probe study of Ru isotopes in refractory metal nuggets from an Allende CAI produced similar results, however, at much lower (% level) precision (Hutcheon et al., 1987). Two unpublished studies reported variable positive deviations of ^{98}Ru of up to 40ε units in IIA, IIIA and IVB iron meteorites (Smoliar, 1998), and possibly in the IVA iron meteorite Gibeon (Yin, 1995). In addition, Yin (1995) found a small positive deviation of $1.1 \pm 0.5\varepsilon$ for ^{99}Ru in the magnetic fraction of the carbonaceous chondrite Maralinga, but no deviation in the whole rock. Both studies employed negative TIMS (N-TIMS), which yielded better sensitivity than P-TIMS.

Two arguments suggest that these results could be valid. First, the ^{53}Mn–^{53}Cr systematics of IIIA iron meteorites suggests that they crystallized within 5 Ma of the angrites (4558 Ma, Lugmair and Galer, 1992; Lugmair et al., 1992; Nyquist et al., 1994), placing their formation very early in solar system chronology. Second, some of the metal that segregated into asteroidal cores may have undergone very early processing and element fractionation in the solar nebula (Kelly and Larimer, 1977). If ^{98}Tc and ^{99}Tc were extant, anomalies of ^{98}Ru and ^{99}Ru would develop, given sufficient changes in Tc/Ru.

New data on terrestrial Ru from various sources, chondrites and IIAB and IIIAB iron meteorites show that the Ru isotopic compositions of all these materials are identical within analytical uncertainties (Becker and Walker, 2001; this work). Here, we will focus on the ^{98}Ru and ^{99}Ru data and the implications for the abundance of ^{98}Tc and ^{99}Tc, and Tc–Ru fractionation in the early solar system. An accompanying study of Ru isotopes by multi-collector ICP-MS has confirmed the present results (Becker et al., 2002).

2. Analytical techniques

Small pieces of iron meteorites (1.540–2.708 g) were cut using a Leco 'Vari-cut' saw with diamond wafering blades designated for the various Re and Os concentration ranges in iron meteorites, and using deionized water as coolant. The iron meteorite pieces

were abraded using carborundum and briefly leached in 11 M HCl. After dissolution in 20 ml of concentrated HCl, trace amounts of carbon remained as insoluble residue. The supernatant was dried and redissolved in 0.1 M HCl. The platinum-group elements (PGE) were separated from the Fe–Ni matrix using 2 ml cation exchange columns (AG50-X8, 100–200 mesh) and 0.1 M HCl. Ruthenium was separated from the other PGE and interfering elements such as Mo by a modified microdistillation technique. A 2:1 mixture of CrO_3 dissolved in 19 N H_2SO_4 and concentrated $HClO_4$ was used as the oxidant. RuO_4 was distilled at 80 °C for 2 h and collected in 3% H_2O_2. USNM Allende standard reference powder (USNM 3529 Split 15, Pos. 8, 1.0304 g) and a piece of Allegan (USNM 3279, 1.0463 g), ground in an agate mortar, were digested using a NaOH–Na_2O_2 fusion technique described in detail by Morgan and Walker (1989). This technique has the advantage that it results in total digestion of the chondrites, including phases that are difficult to dissolve such as spinel and PGE alloys. Because of the large amount of chondrite samples analyzed in this study, the quantities of reagents were doubled and the fusion temperature was held at 600 °C for 60 to 90 min. After digestion, the cake was dissolved in H_2SO_4 and distilled in a conventional distillation apparatus using a 20% solution of $NaBrO_3$ as the oxidant and 8.8 M HBr as the trap solution. The Ru fraction of the chondrites was also further cleaned by microdistillation. After microdistillation, 5 µl of 13.5 M HNO_3 was added to the peroxide solution and carefully evaporated to dryness under a heat lamp. The Ru fraction was loaded in 13.5 M HNO_3 on outgassed Pt filaments (2.6 A, 1 h), and covered with a mixture of $Ba(OH)_2$ and NaOH. The Ru loading blank for this technique is < 30 fg. Total chemistry Ru blanks for the iron meteorite and chondrite chemistries are 1.8 and 149 pg, respectively, and are insignificant.

Samples were run on the Sector 54 multi-collector thermal ionization mass spectrometer at the Isotope Geochemistry Laboratory (IGL), University of Maryland. Ruthenium was measured in the negative mode as RuO_3^- with a pressure of $2.7–4.5 \times 10^{-6}$ mbar maintained by leaking O_2 into the source. Filament temperatures at running conditions were in the 850–870 °C range. Typical ion beams for standards and most samples (see Table 2) were $0.8–1.4 \times 10^{-11}$ A

for ^{102}Ru for at least several hours. Because all Ru masses and a number of interfering isotopes were measured, a three-cycle measurement routine was employed. Two hundred individual scans were acquired per run. All masses relevant for the present study (144, 145, 146, 147, 148, 149, 150) were measured in the first cycle. Molybdenum is a major interference on masses 144, 146, and 148, and was monitored via mass 145 (^{97}MoO$_3^-$). The Mo interference, primarily from the Pt filament, must be kept at a very low level in order to permit a reliable correction. In this study, ^{97}Mo/^{101}Ru was 0.000019 ± 7 for the standard ($n = 66$), and samples lie within error of that value. Interference corrections were made using high-precision Mo isotopic abundances from Qi-Lu and Masuda (1994). Furthermore, BaO$^-$ is monitored on mass 151 (second cycle) in order to account for potential interferences on masses 146, 148, 150 and 152. These interferences were very small or insignificant. Oxygen corrections were made using ^{17}O/^{16}O and ^{18}O/^{16}O values from Nier (1950), which overlap with O isotopic compositions periodically determined from ReO$_4^-$ measurements at UMD. As in most previous studies (Huang and Masuda, 1997; Poths et al., 1987; Yin, 1995), instrumental mass fractionation was corrected to ^{96}Ru/^{101}Ru using the value 0.324851 (Poths et al., 1987) and an exponential mass fractionation law (Russell et al., 1978). Mass bias was typically $1–2.5‰$ per amu. During the initial period of this work, we used ^{100}Ru/^{101}Ru to correct for mass bias (Becker and Walker, 2000). It will be discussed later why this ratio does not represent a satisfactory means for mass bias correction of ^{98}Ru/^{101}Ru and ^{99}Ru/^{101}Ru.

In order to test our ability to measure small differences in ^{98}Ru and ^{99}Ru isotopic abundances, gravimetric mixtures of normal Ru and isotopically enriched Ru were made. Isotopic tracers enriched in ^{98}Ru (89.34 at.%) and ^{99}Ru (97.69 at.%) were obtained from Oak Ridge National Laboratory, dissolved in Carius tubes, using aqua regia, calibrated using Ru standard solutions, and diluted. Precisely weighed amounts of these dilute tracer solutions were mixed with known amounts of Ru standard solution and equilibrated overnight in Carius tubes and reverse aqua regia at 240 °C. After drying down, a fraction of each mixture was microdistilled and analyzed repeatedly on the mass spectrometer.

3. Results

3.1. Terrestrial Ru standard

The isotopic composition and external precisions for 1 μg of a Ru chloride solution (RuCl$_3$ from Aldrich in 6 M HCl) was monitored between May 1999 and May 2001, and represents our primary reference material ('standard'). The mean ^{98}Ru/^{101}Ru and ^{99}Ru/^{101}Ru over this period of time ($n = 66$) are 0.109548 ± 16 and 0.747778 ± 44, respectively (Table 1, Fig. 1). The isotopic composition of the Aldrich Ru solution agrees with that of other sources of terrestrial Ru analyzed during the course of this study within analytical precision (Becker and Walker, 2001). 2σ external precisions over a 2-year period are ± 1.48ε units (parts in 10,000) for ^{98}Ru/^{101}Ru, and ± 0.59ε for ^{99}Ru/^{101}Ru. External precisions were improved by about a factor of 2 by repeated analysis of samples during shorter periods of time ($n = 4$, $2\sigma_m = ± 0.74\varepsilon$ for ^{98}Ru/

^{101}Ru, and ± 0.30ε for ^{99}Ru/^{101}Ru). Table 1 shows the data of this study in comparison to high-precision Ru isotopic data from previous studies obtained by positive (P-TIMS), negative thermal ionization mass spectrometry (N-TIMS), and our recent study by multi-collector ICP-MS (Becker et al., 2002). The agreement is generally within analytical uncertainties. Discrepancies are noted with the ^{98}Ru/^{101}Ru value from Yin (1995), which appears too high by about 1ε unit, and the ^{99}Ru/^{101}Ru value of Smoliar (1998), which, for unknown reasons, is lower than other results by 3ε units. In a recent abstract, Chen and Papanastassiou (2002) reported ^{98}Ru/^{101}Ru data (also N-TIMS) for their standard that is 6–12ε units lower than our and other previously published data. They attribute this difference to a much smaller Mo interference ($< 0.4\varepsilon$) compared to previous work. We note that the ^{98}Mo correction we apply to our ^{98}Ru/^{101}Ru value on average corresponds to only 4.4 ± 1.6ε units. While this correction is significant, it is not excessive and the discrepancy to the much lower ^{98}Ru/^{101}Ru reported by Chen and Papanastassiou (2002) is difficult to explain. We also note that an independent study of the isotopic composition of terrestrial and meteoritic Ru by multi-collector ICP-MS supports our and most previous N- and P-TIMS results (Becker et al., 2002). With ^{97}Mo/^{101}Ru as low as 0.000002 for individual runs (mean 0.000008 ± 10), the ICP-MS study showed much lower Mo interference levels than the present N-TIMS study. The corrected mean ^{98}Ru/^{101}Ru of 0.109548 ± 18 (2σ) obtained by ICP-MS overlaps with the present, and most previous N- and P-TIMS results (Table 1), in spite of the different magnitudes of Mo corrections.

In order to demonstrate that ε level deviations of ^{98}Ru and ^{99}Ru can be detected by N-TIMS, known quantities of a Ru standard solution were mixed and equilibrated with precisely weighed aliquots of calibrated, dilute ^{98}Ru and ^{99}Ru spikes. In Fig. 2, and in subsequent figures, measured ^{98}Ru/^{101}Ru and ^{99}Ru/^{101}Ru values are normalized to the mean of the standard and are shown in the epsilon notation (e.g., ε^{98}Ru= $(^{98}$Ru/^{101}Ru$_{sample}$/^{98}Ru/^{101}Ru$_{standard} - 1) \times 10^4$). For ^{98}Ru, deviations at the 1ε level can be resolved, whereas for ^{99}Ru, deviations by 0.5 and 1ε are clearly resolved (Fig. 2). The mass spectrometric data show a tendency towards slightly too high values compared to the gravimetric data (ca. 0.3–0.5ε for ^{98}Ru and ca. 0.2ε

Table 1
^{98}Ru/^{101}Ru and ^{99}Ru/^{101}Ru data for terrestrial Ru

Date and data source	^{98}Ru/^{101}Ru	^{99}Ru/^{101}Ru
Aldrich Ru (III) in 6 M HCl ("standard") this work		
5/28/1999–2/22/2000 ($n=27$)	0.109546 ± 14	0.747789 ± 46
6/8/2000–7/24/2000 ($n=15$)	0.109544 ± 17	0.747775 ± 30
7/31/2000–8/24/2000 ($n=4$)	0.109555 ± 14	0.747775 ± 23
8/31/2000–1/2/01 ($n=14$)	0.109552 ± 18	0.747776 ± 31
5/1/01–5/14/01 ($n=6$)	0.109548 ± 9	0.747748 ± 45
5/28/1999–5/14/01 (n=66)	0.109548 ± 16	0.747778 ± 44
ε units ± 2σ	0.00 ± 1.48	0.00 ± 0.59
ε units ± 2σ_m (n=4)	0.00 ± 0.74	0.00 ± 0.30
Literature data		
Poths et al., 1987[a]	0.109550 ± 28	0.747757 ± 49
Yin, 1995[b]	0.109598 ± 11	0.747769 ± 48
Huang and Masuda, 1997[b]	0.109543 ± 26	0.747828 ± 75
Smoliar, 1998[b]	0.109550 ± 10	0.747570 ± 20
Becker et al., 2002[c]	0.109548 ± 18	0.747736 ± 87

n, number of runs. Errors of isotopic ratios refer to the last digits. 2σ errors of the means of multiple runs of the Aldrich Ru "standard" solution and the literature data are 2σ external precisions. $2\sigma_m$ ($n=4$) is the estimated external precision of quadruplicate analysis of standard and samples. ε is the deviation from the mean of the Aldrich standard (see text). Data of the present study normalized to ^{96}Ru/^{101}Ru = 0.324851 (Poths et al., 1987). For references, see text.
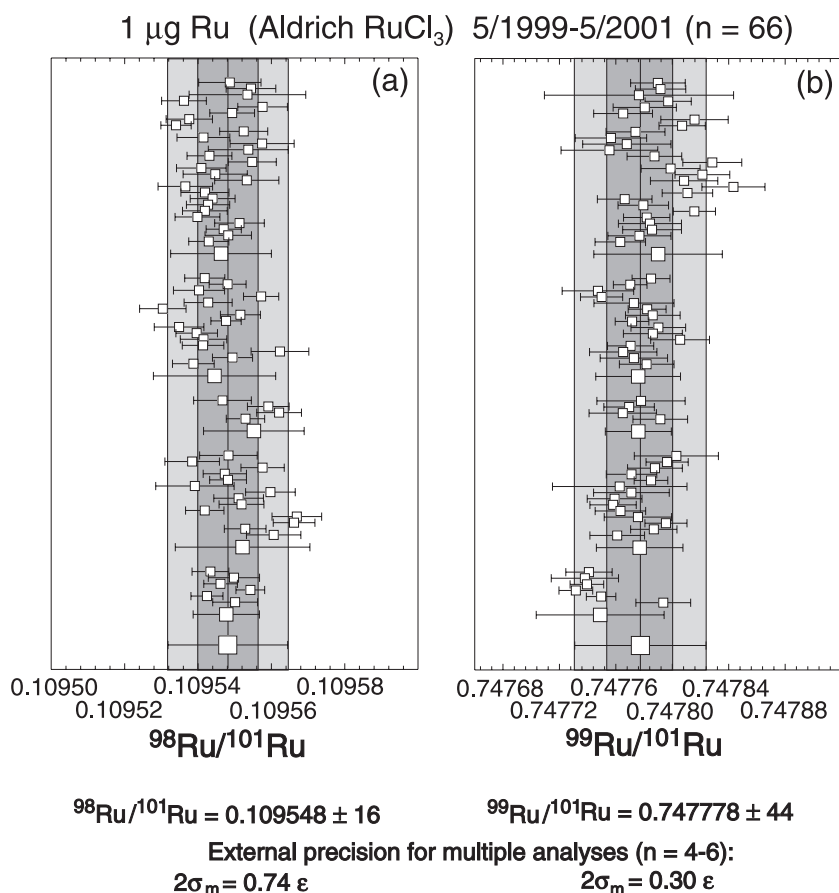[a] P-TIMS.
[b] N-TIMS.
[c] MC ICP-MS.

Fig. 1. $^{98}Ru/^{101}Ru$ (a) and $^{99}Ru/^{101}Ru$ (b) data for 1 µg of Aldrich Ru chloride in 6 M HCl, analyzed between 5/1999 and 5/2001. Smallest symbols are individual runs and their $2\sigma_m$ errors. Intermediate-sized symbols are means and 2σ errors for specific run periods. The largest squares at the bottom and the thin lines and light gray fields represent the grand means of all data and their 2σ uncertainty (For the values, see box). The dark gray fields represent the estimated external precisions for multiple analyses ($n = 4-6$) of standard and samples ($2\sigma_m$, values in the box are given in ε units = parts in 10,000). All data were normalized to $^{96}Ru/^{101}Ru = 0.324851$ (Poths et al., 1987).

for ^{99}Ru). It should be noted that these deviations are minor compared to the differences of $6-12\varepsilon$ units for $^{98}Ru/^{101}Ru$ reported by Chen and Papanastassiou (2002), relative to other data.

3.2. Iron meteorites and chondrites

The magmatic IIAB iron meteorites Negrillos, Bennett County, Coahuila, Filomena and Old Woman, and the IIIAB iron meteorites Casas Grandes and Costilla Peak were analyzed for their Ru isotopic compositions. The Ru concentrations in these samples range between 26 and 10 ppm (Pernicka and Wasson,

1987). The Ru concentration in Old Woman has not been determined. It may be somewhat lower than concentrations in less evolved IIAB iron meteorites because of the apparent compatibility of Ru with solid metal. In most cases, µg quantities of Ru were analyzed in individual runs of iron meteorites. A split of a standard reference powder of the carbonaceous chondrite Allende (CV3) and the ordinary chondrite Allegan (H5) were analyzed as well. Ruthenium concentrations in chondrites are much lower than in most magmatic iron meteorites. Allende contains about 0.8 ppm Ru (Jochum, 1996; Horan et al., in press). The Ru concentration in Allegan is unknown.
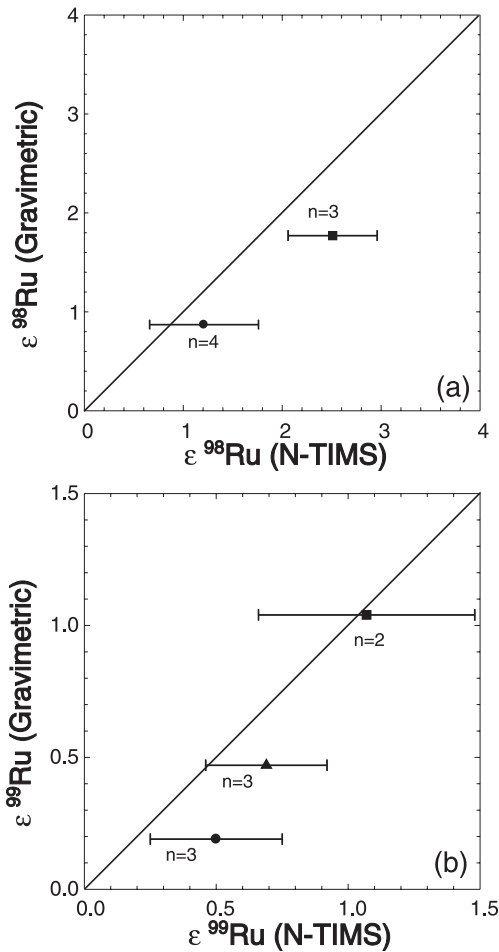
Fig. 2. Gravimetric mixtures of dilute ^{98}Ru (a) and ^{99}Ru (b) spikes and calibrated Alfa–Aesar ICP Ru standard solution vs. mass spectrometric results. Shown are the means of n analyses for each mixture and $2\sigma_m$ uncertainties. The ε representation indicates parts in 10,000 deviation of the measured and gravimetric values from the mean of the pure standard. Deviations $>1\varepsilon$ for ^{98}Ru and $>0.5\varepsilon$ for ^{99}Ru are clearly resolvable.

($n=1-11$) of the iron meteorites are 0.87 ± 0.31 (Negrillos), 0.02 ± 0.93 (Bennett County, IIA), 0.23 ± 0.80 (Coahuila), 1.93 ± 1.41 (Single analysis of Filomena), 1.14 ± 0.99 (Old Woman), 1.10 ± 1.17 (Casas Grandes), and -0.06 ± 0.28 (Costilla Peak), respectively. All iron meteorites overlap with the Aldrich standard within external precision. It should be noted that Negrillos, Filomena, Old Woman and Casas Grandes show a slight displacement towards
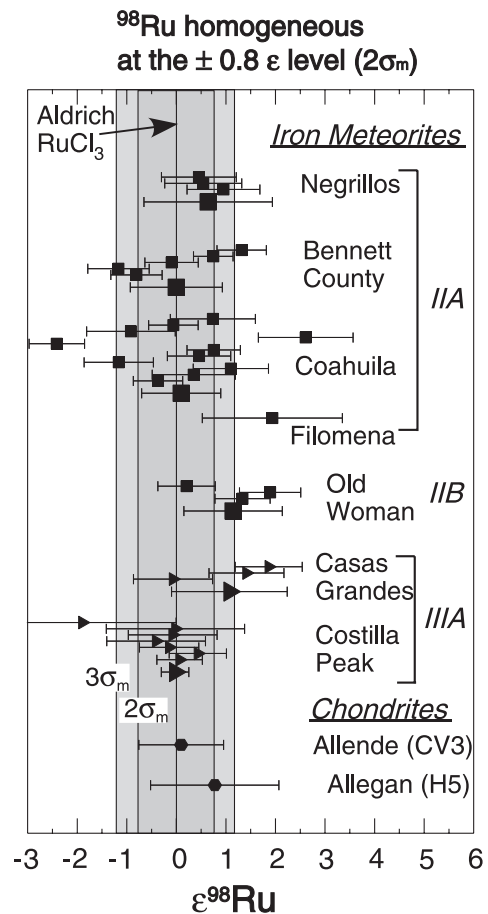

Fig. 3. ε^{98}Ru data for iron meteorites and chondrites. Small symbols are individual runs, large symbols are the means of these runs. Error bars are $2\sigma_m$. Data normalized to the means of the Aldrich standard during specific run periods (ε^{98}Ru $= 0$). The dark gray and light gray fields are $2\sigma_m$ and $3\sigma_m$ uncertainties for four to six analyses of standards and samples. Both the iron meteorite data and the chondrite data overlap with the Aldrich standard at the 0.8ε level.

Other H-chondrites typically contain between 1.1 and 1.4 ppm Ru (Wasson and Kallemeyn, 1988; Horan et al., in press). The smaller quantities of Ru in chondrites (0.3–0.5 μg per run) resulted in somewhat poorer in-run precisions. Fig. 3 shows the deviation of the ^{98}Ru/^{101}Ru data of the meteorites from the mean of the Aldrich standard in the form of ε^{98}Ru data for individual runs and the means of multiple runs for each sample (Table 2). For ε^{98}Ru, the means of n analyses

Table 2
$^{98}Ru/^{101}Ru$ and $^{99}Ru/^{101}Ru$ data for iron meteorites and chondrites

Date	^{102}Ru (mV)	$^{98}Ru/^{101}Ru$	$^{99}Ru/^{101}Ru$
Iron meteorites			
Negrillos (IIAB) USNM 1222			
02/17/2000	1100−930	0.109555 ± 8	0.747781 ± 31
03/02/2000	860−760	0.109556 ± 9	0.747771 ± 27
03/02/2000	900−860	0.109560 ± 8	0.747787 ± 34
Mean		0.109557 ± 3	0.747780 ± 9
ε		0.87 ± 0.31	0.02 ± 0.12
Bennett County (IIAB) USNM 1199			
03/01/2000	1100−1600	0.109559 ± 5	0.747744 ± 21
03/02/2000	1300	0.109553 ± 4	0.747780 ± 13
07/24/2000	1100−1200	0.109542 ± 6	0.747770 ± 15
08/24/2000	1300−1500	0.109541 ± 7	0.747723 ± 27
08/22/2000	1300−1400	0.109545 ± 6	0.747781 ± 25
Mean		0.109548 ± 7	0.747760 ± 23
ε		0.02 ± 0.93	− 0.25 ± 0.31
Coahuila (IIAB) USNM 2725			
02/03/2000	600−650	0.109554 ± 9	0.747786 ± 18
02/07/2000	1000−1100	0.109545 ± 5	0.747747 ± 15
02/04/2000	500−540	0.109536 ± 10	0.747776 ± 19
02/08/2000	420−590	0.109575 ± 10	0.747784 ± 18
07/17/2000	950−740	0.109526 ± 6	0.747766 ± 13
09/06/2000	890−830	0.109560 ± 6	0.747761 ± 15
07/23/2000	1200−1300	0.109549 ± 7	0.747754 ± 28
08/22/2000	1300−2100	0.109542 ± 8	0.747743 ± 34
07/24/2000	1000−1100	0.109556 ± 8	0.747763 ± 30
09/05/2000	650−590	0.109556 ± 9	0.747740 ± 25
08/23/2000	1300−1400	0.109551 ± 5	0.747761 ± 21
Mean		0.109550 ± 8	0.747762 ± 9
ε		0.23 ± 0.80	− 0.22 ± 0.10
Filomena (IIAB) USNM 1334			
05/01/01	520−280	0.109569 ± 15	0.747710 ± 57
ε		1.93 ± 1.41	− 0.92 ± 0.76
Old Woman (IIAB) USNM 6359			
05/02/01	880−740	0.109550 ± 6	0.747709 ± 21
05/02/01	1000−950	0.109568 ± 7	0.747773 ± 27
05/02/01	910−830	0.109562 ± 6	0.747777 ± 19
Mean		0.109560 ± 11	0.747753 ± 44
ε		1.14 ± 0.99	− 0.34 ± 0.59
Casas Grandes (IIIAB) USNM 369			
02/16/2000	790−800	0.109567 ± 7	0.747783 ± 25
03/01/2000	1000−780	0.109562 ± 8	0.747757 ± 33
08/31/2000	1700−1200	0.109551 ± 9	0.747753 ± 39
Mean		0.109560 ± 9	0.747764 ± 19
ε		1.10 ± 1.17	− 0.19 ± 0.20
Costilla Peak (IIIA) USNM 702			
02/16/2000	700−750	0.109546 ± 10	0.747783 ± 40
07/13/2000	1000−950	0.109540 ± 11	0.747766 ± 39
07/14/2000	940−860	0.109543 ± 7	0.747757 ± 18
07/23/2000	1200−1100	0.109550 ± 6	0.747758 ± 24
07/30/2000	1200	0.109556 ± 5	0.747761 ± 16
Mean		0.109547 ± 6	0.747765 ± 10
ε		− 0.06 ± 0.28	− 0.18 ± 0.06

Table 2 (*continued*)

Date	^{102}Ru (mV)	$^{98}Ru/^{101}Ru$	$^{99}Ru/^{101}Ru$
Chondrites			
Allende (CV3) USNM 3529			
05/09/01	1000−570	0.109549 ± 9	0.747729 ± 40
ε		0.09 ± 0.85	− 0.66 ± 0.54
Allegan (H5) USNM 3279			
05/09/01	400−320	0.109556 ± 14	0.747749 ± 36
05/09/01	280−190	0.109487 ± 23	0.747786 ± 48
Mean		0.109522 ± 69	0.747768 ± 37
ε		− 2.37 ± 4.43	− 0.15 ± 0.49

2σ errors for individual runs are in-run errors. $2\sigma_m$ errors are 2σ errors of the mean of multiple runs, divided by the square root of the number of runs. ε values are deviations from the mean of the Aldrich Ru standard (Table 1). All data normalized to $^{96}Ru/^{101}Ru = 0.324851$.

positive $\varepsilon^{98}Ru$. However, because the $2\sigma_m$ uncertainty on the means of these samples overlap with the standard, and the results on the spike-standard mixtures hint at a slight overestimate of deviations (Fig. 2), these iron meteorites show no resolvable deviation from the standard. Two individual runs for Coahuila show a relative large negative or positive deviation for $\varepsilon^{98}Ru$, relative to the mean of Coahuila, which is similar to the standard value (Table 2). We attribute this to the low signal intensities (400−500 mV ^{102}Ru) during these runs, and observed a similar offset for a low-intensity run of Filomena and the chondrite Allegan (Fig. 3). Individual runs of the chondrites Allende and Allegan also overlap with the Aldrich standard (Fig. 3, Table 2). The second run of Allegan is not shown in this diagram because modest signal intensity resulted in a large error on $^{98}Ru/^{101}Ru$ (Table 2).

Fig. 4 shows the deviation of the $^{99}Ru/^{101}Ru$ data of the meteorites from the mean of the Aldrich standard in the form of $\varepsilon^{99}Ru$ data for individual runs and the means of multiple runs for each sample (See also Table 2). For $\varepsilon^{99}Ru$, the means of n analyses ($n = 1-11$) of the iron meteorites are 0.02 ± 0.12 (Negrillos), -0.25 ± 0.31 (Bennett County), -0.22 ± 0.10 (Coahuila), -0.92 ± 0.76 (Single analysis of Filomena), -0.34 ± 0.59 (Old Woman), -0.19 ± 0.20 (Casas Grandes), and -0.18 ± 0.06 (Costilla Peak), respectively. All iron meteorites overlap with the Aldrich standard within external precision. The same is true for the analyses of the chondrites Allende and Allegan, which, because of smaller beam intensities than for the
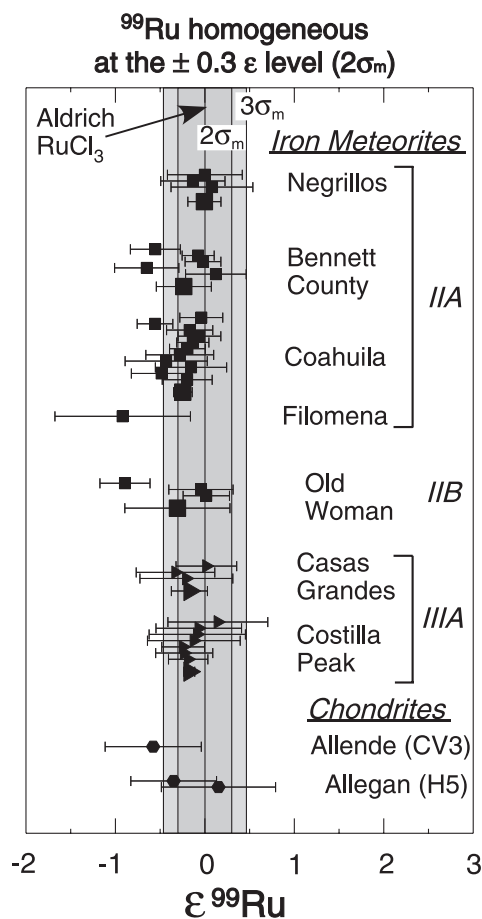
Fig. 4. ε^{99}Ru data for iron meteorites and chondrites. Symbols and uncertainties as in Fig. 3. Iron meteorites and the chondrite data overlap with the Aldrich standard at the $\pm 0.3\varepsilon$ level.

iron meteorites, show somewhat larger uncertainties for in-run precisions.

4. Discussion

4.1. Homogeneous ^{98}Ru and ^{99}Ru in solar system materials

The ^{98}Ru/^{101}Ru and ^{99}Ru/^{101}Ru ratios for IIAB and IIIAB magmatic iron meteorites and the chondrites Allende and Allegan overlap with terrestrial Ru within external precisions. In these materials, ^{98}Ru and ^{99}Ru are homogeneous at the ± 0.8 and $\pm 0.3\varepsilon$ levels, respectively. Abundances of the stable isotopes of Ru

in all samples also agree within error (2σ) with the terrestrial values (Becker and Walker, 2001). These results are consistent with a previous study of the Ru isotopic composition of CAIs from Allende and Leoville that reported homogeneous ^{98}Ru and ^{99}Ru at the 10 and 2.6ε levels, respectively (Poths et al., 1987), albeit at a much higher level of precision.

The new results, compared to our preliminary results that showed apparent small positive deviations of ^{98}Ru and ^{99}Ru in the iron meteorites (Becker and Walker, 2000), reflect improved fractionation correction (normalizing to ^{96}Ru/^{101}Ru instead of ^{100}Ru/^{101}Ru) and signal intensity. If normalized to ^{100}Ru/^{101}Ru, the Ru isotopic data for most meteorites show reproducible positive deviations for ^{96}Ru, ^{98}Ru and ^{99}Ru, and negative deviations for ^{102}Ru, relative to the standard. These apparent deviations disappear, when the data are normalized to ^{96}Ru/^{101}Ru. The differences may reflect the narrow mass range covered by ^{100}Ru/^{101}Ru and the fact that ^{100}Ru and ^{101}Ru lie outside the mass range of interest. Because ^{96}Ru/^{101}Ru covers a much larger mass range and its mean mass (98.5 amu) lies between ^{98}Ru and ^{99}Ru, this ratio, when applied with the exponential or power law, provides the closest approximation of mass discrimination affecting samples and standards. Similar observations were made in recent Ru and Nd high-precision isotopic work by multi-collector ICP-MS, where mass discrimination is much larger, and the proper choice of the normalization ratio is even more important (Becker et al., 2002; Vance and Thirlwall, in press). Our current data for Negrillos and Casas Grandes do not confirm an earlier report suggesting positive deviations of ^{98}Ru in these iron meteorites at the 10 and 40ε level, respectively (Smoliar, 1998). It is likely that the data obtained by Smoliar (1998) reflect analytical problems with the Mo interference correction and mass bias correction, using ^{100}Ru. Positive deviations of ^{98}Ru for the IVA iron meteorite Gibeon and a small positive deviation in ^{99}Ru in metal from the carbonaceous chondrite Maralinga (Yin, 1995) could also reflect analytical problems, because the Mo correction indirectly affects other isotopes via the mass bias correction from ^{96}Ru. Our previous results on aliquots of Old Woman that were not highly purified via microdistillation showed a -1.4ε deviation for ^{99}Ru that was accompanied by positive deviations in ^{102}Ru and ^{104}Ru (Becker and Walker, 2001). This indicates a

mass bias effect that could not be corrected appropriately, because an unidentified interference on mass 96 may have compromised the mass fractionation correction in this sample. In contrast, highly purified aliquots of Old Woman show normal abundances of ^{99}Ru (Fig. 4).

4.2. $^{98}Tc-^{98}Ru$ and $^{99}Tc-^{99}Ru$ evolution models

In this and the following sections, we assess the requirements for the development of ^{98}Ru and ^{99}Ru anomalies. These are: (1) sufficient amounts of ^{98}Tc and ^{99}Tc must have been present in the early solar system; (2) significant fractionation of Tc/Ru in two or more reservoirs must occur while ^{98}Tc and ^{99}Tc are still extant; and (3) these reservoirs must remain physically separated from the moment Tc/Ru fractionation occurred.

Fig. 5 shows simple two-stage evolution models for ^{98}Ru and ^{99}Ru in comparison to our current mass spectrometric resolution. The ^{98}Ru/^{101}Ru and ^{99}Ru/^{101}Ru data were normalized to a nominally chondritic reservoir (Aldrich standard) and the evolution curves are shown in the ε notation as a function of time after injection and mixing of ^{98}Tc and ^{99}Tc into the proto-solar molecular cloud. The models assume a factor 2 increase of Tc/Ru during the fractionation event (see next section) and solar system initial ratios of ^{99}Tc/^{100}Ru$_{\odot i} = 3.4 \times 10^{-5}$ (Wasserburg et al., 1994) and ^{98}Tc/^{96}Ru$_{\odot i} = 2 \times 10^{-5}$ (see discussion below). The half-lives were taken from the Table of the Isotopes (Firestone and Shirley, 1996). In this context, it should be noted that a recent effort (Kobayashi et al., 1993) to re-determine the half-life of ^{98}Tc suggests that it may be longer (~ 10 Ma) than the accepted value of 4.2 Ma. Individual curves show how deviations in ε^{99}Ru and ε^{98}Ru develop as a function of time in cases for which the fractionation event occurred 0.01, 0.1, and 0.5 Ma, and 0.01, 0.1, 0.5, 1, and 2 Ma after the parent isotopes were injected into the proto-solar cloud, respectively.

Most ^{99}Tc is believed to form in s-process chains (e.g., Schatz, 1983). Evidence for its recent production can be found in spectra of certain types of red giant stars (Merrill, 1952). Abundance estimates from spectroscopic studies (Schatz, 1983; Smith and Lambert, 1988) and production models for the s-process (Wasserburg et al., 1994) yield comparable estimates
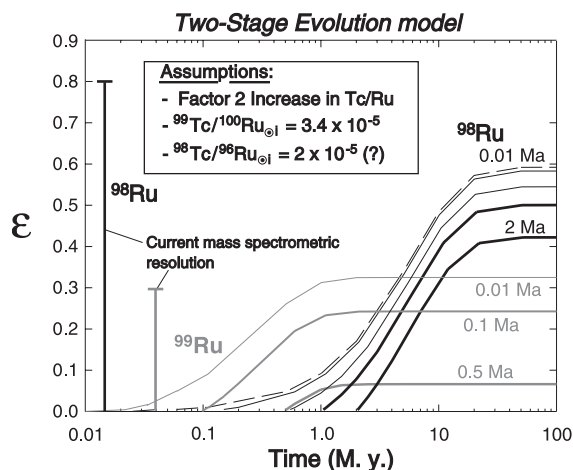

Fig. 5. Two-stage evolution model for ^{98}Ru (black curves) and ^{99}Ru (gray curves) in comparison to the current mass spectrometric resolution of $\pm 0.8\varepsilon$ for Ru and $\pm 0.3\varepsilon$ for ^{99}Ru (bars). The ^{98}Ru/^{101}Ru and ^{99}Ru/^{101}Ru data were normalized to the Aldrich standard and the evolution curves are shown in the epsilon notation as a function of time after injection and mixing of ^{98}Tc (Half-life = 4.2 Ma?) and ^{99}Tc (Half-life = 0.21 Ma) into the presolar molecular cloud. Individual curves show how deviations develop as a function of time in cases for which a Tc/Ru fractionation event occurred between 0.01 and 0.5 Ma (ε^{99}Ru), and between 0.01 and 2 Ma (ε^{98}Ru) after injection of Tc. The models assume a factor 2 (100%) increase of Tc/Ru during the fractionation event (see text for more details). ^{99}Tc/^{100}Ru$_{\odot i}$ represents the bulk solar system initial of this s-process isotopic ratio, predicted by Wasserburg et al. (1994). The p-process ratio ^{98}Tc/^{96}Ru$_{\odot i}$ is unknown. The value used here is a maximum value that is consistent with the absence of resolvable deviations in ^{98}Ru.

for the s-process production ratio ^{99}Tc/^{100}Ru$_p$ (0.16– 0.18). Using these estimates, and constraints for the abundance of other s-process isotopes, Wasserburg et al. (1994) predicted a range of values for ^{99}Tc/^{100}Ru$_{\odot i}$ between 2.3×10^{-5} and 3.9×10^{-5}, for various production, injection and mixing scenarios involving the He shell of AGB stars and the proto-solar molecular cloud. In Fig. 5, a value of 3.4×10^{-5} for ^{99}Tc/^{100}Ru$_{\odot i}$ is used for illustrative purposes. In order to develop ^{99}Ru anomalies at the 1ε level, fractionation would have to occur early (within ~ 10,000 years) and the change in Tc/Ru would have to be on the order of a factor of 4. More realistic values for the change in Tc/Ru (< 2 as in Fig. 5) require an analytical resolution of better than 0.1ε unit to allow positive identification of ^{99}Ru deviations. Later fractionation events require proportionately larger Tc/Ru fractionations.

The initial solar system abundance of ^{98}Tc is unknown. Experimental studies and nuclear properties of this odd–odd isotope suggest that it should be rare, and may form by proton capture or photodisintegration reactions, involving *s*- and *r*-process seeds, such as ^{98}Mo (Boyd et al., 1955; Schatz, 1983). Such reactions require the high temperatures and short time scales of explosive nucleosynthesis (e.g., Meyer, 1994). Proposed sites and processes may be the O–Ne layers of massive stars during Type II supernovae and associated photodisintegration of neutrons (γ, *n*) in *s*-process seeds (Rayet et al., 1995), or proton capture reactions during the explosion of white dwarfs (Howard and Meyer, 1993; Howard et al., 1991). Estimates of the production ratio ^{98}Tc/^{92}Mo$_p$ for these two sites were given as 3×10^{-5} to 2×10^{-4} (Type II supernovae, Rayet et al., 1995) and 10^{-4} (Type Ia supernovae, Howard and Meyer, 1993), respectively. Using the estimates for ^{98}Tc/^{92}Mo$_p$, the ratios of overproduction factors F^{92}Mo/F^{96}Ru from the Type II supernova models of Rayet et al. (1995), ranging between 0.78 and 1.44, and a solar ^{92}Mo/^{96}Ru$_\odot$ of 5.03 (Anders and Grevesse, 1989), we obtain $1.2 \times 10^{-4} < {}^{98}$Tc/^{96}Ru$_p < 1.5 \times 10^{-3}$ for these scenarios. Overproduction factors *F* represent the total mass fraction of a particular nuclide produced in the production zones of an exploding star, normalized to the solar mass fraction of the nuclide. The low yields for ^{98}Tc relative to other *p*-nuclides suggest that most solar ^{98}Ru must come from other progenitors. If short-lived nuclides such as ^{26}Al, ^{53}Mn and ^{60}Fe were indeed injected into the solar cloud during a Type II supernova trigger event (Cameron et al., 1997), their production ratios and solar system initial abundance ratios obtained from meteoritic evidence yield a dilution factor that can be used to estimate values for ratios that are less well constrained such as ^{98}Tc/^{96}Ru$_{\odot i}$. The dilution factor $M_{SNE}/M_\odot$ (ratio of the mass of supernova ejecta, relative to the total mass of the presolar cloud) would be about 10^{-4} for instantaneous injection into the cloud, in order to satisfy the constraints on ^{53}Mn/^{55}Mn$_\odot$ and other short-lived decay schemes (Wasserburg et al., 1996). This level of dilution results in very low ^{98}Tc/^{96}Ru$_{\odot i}$ of ca. 10^{-8} to 10^{-7}. This level is sufficiently low that only very large fractionations in Tc/Ru on the order of factors of 200 to 2000 would generate detectable (>1ε unit) deviations in ^{98}Ru.

It should be noted that the production models considerably underestimate abundances of *p*-nuclei in the Mo–Tc–Ru region, compared to such nuclei in other mass regions and solar values (Rayet et al., 2001). Evidence for extant ^{92}Nb in the early solar system has been used to argue that the *p*-process production ratio ^{92}Nb/^{92}Mo$_{\odot i}$ should be 10 to 50 times higher than results calculated for most Types Ia and II supernova sources (Yin et al., 2000). However, other results for the initial ^{92}Nb/^{93}Nb of the solar system seem to agree with the low abundances predicted by theoretical models (Schönbächler et al., 2002). Other sites have been suggested that may have the high temperatures, proton densities and *s*-process seed availability to produce the light *p*-nuclides and their abundance systematics by rapid proton capture (Hencheck, 1995). Many assumptions in these models await further evaluation. Because of these uncertainties, a maximum value for the *p*-process initial solar system ratio ^{98}Tc/^{96}Ru$_{\odot i}$ of ~ 2×10^{-5} was chosen in Fig. 5, the basis being the absence of deviations in ^{98}Ru at the $\pm 0.8\varepsilon$ level.

4.3. Constraints on Tc/Ru fractionation in the early solar system

The chemical fractionation of Tc from Ru during early solar system processing is one of the key input parameters for any evolution model of the Tc–Ru chronometers. Fractionation of Tc/Ru may occur in four different ways: (1) during condensation and evaporation processes because of the different volatility of Tc and Ru; (2) during metal–silicate segregation because of different metal–silicate partition coefficients; (3) during crystallization of a core because of different solid metal–liquid metal partition coefficients; (4) during preferred mobilization of Tc resulting from aqueous alteration at low temperatures and oxidizing conditions.

Condensation and evaporation in the solar nebula may be significant mechanisms for the fractionation of Tc from Ru according to differences in volatility. At 1 bar, Tc has a significantly higher boiling point (4877 °C) than Ru (3900 °C, Handbook of Chemistry and Physics, 1990). The boiling point of Tc is similar to that of Os (5027 °C). Hence, the variability of Os/Ru in bulk chondrites and unequilibrated chondrite components should be a good proxy for the variability of

Tc/Ru. Os/Ru in bulk chondrites ranges between 0.65 and 0.91 (Wasson and Kallemeyn, 1988; Kallemeyn et al., 1994; Jochum, 1996; Horan et al., in press) significantly less than a factor of 2 change in the ratio. Os/Ru in calcium–aluminum-rich inclusions (CAIs) from carbonaceous chondrites also varies significantly less than a factor of 2 (Mason and Taylor, 1982; Palme et al., 1994). Tiny refractory metal nuggets in CAIs show somewhat larger variations in Os/Ru of up to a factor of 4 (Sylvester et al., 1990), however, it is not clear whether these variations always reflect volatility-controlled processes. Alternatively, they might reflect secondary alteration (see below, and Blum et al., 1989). Other components of unequilibrated chondrites such as metal also show little variation in Os/Ru (Kong and Ebihara, 1997). In summary, volatility-controlled Tc/Ru fractionation under reducing conditions of the solar nebula will likely produce much less than a factor of 2 variability in this ratio.

The fractionation of Tc from Ru during metal–silicate partitioning is poorly constrained. The HSE are defined by metal–silicate partition coefficients $(D^{me/si}) > 10^4$. Its position in the periodic table and the similarity of Tc to other HSE during metal–sulfide partitioning (see below) suggests that Tc should behave similarly to these elements during metal–silicate segregation. Experimental studies of the metal–silicate partition coefficients of Ir, Os, Re, Pt, and Pd have been plagued by analytical difficulties resulting from nugget effects and the low concentrations of these elements in silicates (e.g., Ertel et al., 2001; O'Neill et al., 1995). At this stage, it cannot be ruled out that large differences may exist for $D^{me/si}$ of different HSE, and that pressure effects may influence $D^{me/si}$ of HSE (Righter and Drake, 1997). Osmium isotopic data for eucrites and diogenites provide a hint for the relative partitioning of Re and Os during low-pressure metal–silicate segregation on the HED parent body. Low Os abundances in eucrites and cumulate diogenites (Morgan et al., 1978; Birck and Allegre, 1994) suggest near-quantitative removal of HSE during core segregation in the HED parent body. Chondritic to mildly suprachondritic $^{187}Os/^{188}Os$ of eucrites and diogenites (Birck and Allegre, 1994) indicate only a small change of less than a factor of 2 in Re/Os of the residual silicates as a result of metal segregation, and by inference also in segregated bulk metal. These results argue in favor of very limited Tc–Ru fractionation during metal–silicate segregation processes.

Recent high-pressure metal–sulfide partitioning experiments for Tc, Ru and Re indicate that Tc behaves much more like Ru than like Re during crystal–liquid fractionation in a metallic core (Lazar, 2001). The ratio of the metal–sulfide partition coefficients $D^{me/su}(Tc)/D^{me/su}(Ru)$ in these experiments is < 1. This means that initial crystallization of solid metal results in decreased Tc/Ru in solid metal, relative to Tc/Ru in the bulk core. The Earth's upper mantle, represented by our Aldrich standard, has a chondritic Ru isotopic composition. Consequently, ^{98}Ru deviations that developed in solid metal during early metal crystallization in a liquid core with chondritic Tc/Ru should be negative. These effects likely would be miniscule however, even under the most favorable circumstances, such as during very early core formation. $D^{me/su}(Tc)/D^{me/su}(Ru)$ deviates only modestly from unity in the experiments (Lazar, 2001). Consequently, differences in Tc/Ru between early-crystallized metal in an asteroidal core and chondritic materials are significantly less than a factor of 2.

Redox-dependent processes such as aqueous alteration may fractionate Tc/Ru because of the significantly greater stability of oxidized Tc compounds, relative to oxidized Ru compounds. Under these conditions, Tc behaves very similarly to its chemical homologue Re (Greenwood and Earnshaw, 1994). Aqueous alteration and oxidation of metal and sulfides in chondritic parent bodies occurred within the first few Ma of accretion of the protoplanets (Endress et al., 1996). In principle, deviations of ^{98}Ru may have been produced at least on a small scale, if alteration occurred sufficiently early and the extent of fractionation of Tc/Ru was sufficiently large. In this context, Re/Os may be a useful proxy for Tc/Ru because of the chemical similarities during oxidizing conditions. Distinct ranges of Re/Os for different groups of chondrite whole rocks likely represent a primary feature caused by differences in their condensation history (Morgan and Lovering, 1967; Chen et al., 1998; Walker et al., in press). The total range of variability of Re/Os in chondrite whole rocks is much less than a factor of 2. The total variability of Re/Os in CAIs and other components such as chondrules, metal and matrix is also generally less then a factor of 2, much of it reflecting primary differences caused by different

condensation histories or metal−sulfide fractionation (Chen et al., 1998; Becker et al., 2001; Walker et al., in press). Even studies of HSE in alloys and sulfides in CAIs report limited ranges for Re/Os within a factor 2 of the chondritic value (Sylvester et al., 1990). Judging from these results, it is safe to say that redox-dependent fractionation processes such as early aqueous alteration of chondrites or locally variable f_{O^2} in the solar nebula likely did not result in significant Tc/Ru fractionation.

Because volatility-controlled fractionation produced almost certainly much less than a factor of 2 change in Tc/Ru, any deviation in ^{98}Ru and ^{99}Ru due to these processes will be too small to be resolvable (Fig. 5). For instance, a change in Tc/Ru by 50% 10,000 years into the evolution of the nebula would produce only a 0.16ε deviation of ^{99}Ru. These conclusions are consistent with our whole rock results on Allende and Allegan, and the negative results of a Ru isotopic study of CAIs from Allende and Leoville (Poths et al., 1987). The other processes discussed above likely also produced much less than a factor of 2 change in this ratio, the only unknown being metal−silicate segregation.

5. Conclusions

Ruthenium isotopic data for magmatic iron meteorites and two chondrites overlap with terrestrial Ru within 0.8ε units for ^{98}Ru, and within 0.3ε units for ^{99}Ru, respectively. Evolution models that incorporate data on the fractionation of HSE in meteorites and astrophysical models for the initial solar system abundance of s-process ^{99}Tc indicate that the short half-life of the ^{99}Tc−^{99}Ru system requires very early fractionation ($< 10,000$ years) of the parent−daughter ratio in order to produce deviations of 0.3ε units. The limited fractionation of Tc/Ru during early solar system processes may represent the main reason for the absence of resolvable deviations in ^{98}Ru and ^{99}Ru in solar system materials. The lack of deviations in ^{98}Ru suggests that ^{98}Tc/^{96}Ru$_{\odot i}$ must have been less than 2×10^{-5}. Even if explosive nucleosynthesis triggered the collapse of the protosolar molecular cloud (Cameron et al., 1997), and injected fresh-synthesized ^{98}Tc, it appears unlikely that evidence for it can be detected given the limited Tc−Ru fractionation in meteorites and the current analytical resolution.

References

Anders, E., Grevesse, N., 1989. Abundances of the elements: meteoritic and solar. Geochim. Cosmochim. Acta 53, 197−214.

Becker, H., Walker, R.J., 2000. Positive ^{98}Ru and ^{99}Ru anomalies in iron meteorites. Lunar and Planetary Science. Houston, pp. Abstract #1484.

Becker, H., Walker, R.J., 2001. The ^{98}Tc−^{98}Ru and ^{99}Tc−^{99}Ru chronometers: new results on iron meteorites and terrestrial Ru. Eleventh Annual V.M. Goldschmidt Conference. Lunar and Planetary Institute, Houston. pp. Abstract # 3047 (CD-ROM).

Becker, H., Morgan, J.W., Walker, R.J., MacPherson, G.J., Grossman, J.N., 2001. Rhenium−osmium systematics of calcium−aluminium-rich inclusions in carbonaceous chondrites. Geochim. Cosmochim. Acta 65, 3379−3390.

Becker, H., Dalpe, C., Walker, R.J., 2002. High-precision Ru isotopic measurements by multi-collector ICP-MS. Analyst 127, 775−780.

Birck, J.L., Allegre, C.J., 1994. Contrasting Re/Os magmatic fractionation in planetary basalts. Earth Planet. Sci. Lett. 124, 139−148.

Blum, J.D., Wasserburg, G.J., Hutcheon, I.D., Beckett, J.R., Stolper, E.M., 1989. Origin of opaque assemblages in C3V meteorites: implications for nebular and planetary processes. Geochim. Cosmochim. Acta 53, 543−556.

Boyd, G.E., Sites, J.R., Larson, Q.V., Baldock, C.R., 1955. Production and identification of long-lived technetium isotopes at masses 97, 98, and 99. Phys. Rev. 99, 1030−1031.

Cameron, A.G.W., Vanhala, H., Hoeflich, P., 1997. Some aspects of triggered star formation. In: Bernatowicz, T.J., Zinner, E.K. (Eds.), Astrophysical Implications of the Laboratory Study of Presolar Materials. AIP Press, Woodbury (NY) p. 665−693.

Chen, J.H., Papanastassiou, D.A., 2002. NTIMS determination of ruthenium isotopes. 65th Annual Meteoritical Society Meeting. Lunar and Planetary Institute, Houston, pp. CD-ROM Abstract #5180.

Chen, J.H., Papanastassiou, D.A., Wasserburg, G.J., 1998. Re–Os systematics in chondrites and the fractionation of the platinum group elements in the early solar system. Geochim. Cosmochim. Acta 62, 3379–3392.

Endress, M., Zinner, E., Bischoff, A., 1996. Early aqueous activity on primitive meteorite parent bodies. Nature 379, 701–703.

Ertel, W., O'Neill, H.S.C., Sylvester, P.J., Dingwell, D.B., Spettel, B., 2001. The solubility of rhenium in silicate melts: implications for the geochemical properties of rhenium at high temperatures. Geochim. Cosmochim. Acta 65, 2161–2170.

Feitknecht, J., Herr, W., Hoffmeister, W., 1962. Isotopenzusammensetzung von Ruthenium in Meteoriten. Helv. Phys. Acta XXXV, 289–291.

Firestone, R.B., Shirley, V.S., 1996. Table of the Isotopes. Wiley, New York.

Greenwood, N.N., Earnshaw, A., 1994. Chemistry of the Elements. Pergamon, Oxford. 1542 pp.

Hencheck, M., 1995. The rapid hydrogen burning process and the solar abundances of ^{92}Mo, ^{94}Mo, ^{96}Ru and ^{98}Ru. In: Busso, M., Gallino, R., Raiteri, C.M. (Eds.), Nuclei in the Cosmos III. American Institute of Physics, New York, pp. 331–334.

Herr, W., Merz, E., Eberhardt, P., Geiss, J., Lang, C., Signer, P., 1958. Search for decay products of natural technetium. Geochim. Cosmochim. Acta 14, 158.

Horan, M.F., Walker, R.J., Morgan, J.W., Grossman, J.N., Rubin, A.E., 2003. Highly siderophile elements in chondrites. Chem. Geol. (in press).

Howard, W.M., Meyer, B.S., 1993. The p-process and type Ia supernovae. In: Kaeppeler, F., Wisshak, K. (Eds.), Nuclei in the Cosmos. Institute of Physics, Bristol, p. 575.

Howard, W.M., Meyer, B.S., Woosley, S.E., 1991. A new site for the astrophysical gamma-process. Astrophys. J. 373, L5–L8.

Huang, M., Masuda, A., 1997. Measurement of the atomic weight of ruthenium by negative thermal ionization mass spectrometry. Anal. Chem. 69, 1135–1139.

Hutcheon, I.D., Armstrong, J.T., Wasserburg, G.J., 1987. Isotopic studies of Mg, Fe, Mo, Ru and W in Fremdlinge from Allende refractory inclusions. Geochim. Cosmochim. Acta 51, 3175–3192.

Jochum, K.P., 1996. Rhodium and other platinum-group elements in carbonaceous chondrites. Geochim. Cosmochim. Acta 60, 3353–3357.

Kallemeyn, G.W., Rubin, A.E., Wasson, J.T., 1994. The compositional classification of chondrites: VI. The CR carbonaceous chondrite group. Geochim. Cosmochim. Acta 58, 2873–2888.

Kelly, W., Larimer, J., 1977. Chemical fractionations in meteorites: VIII. Iron meteorites and the cosmochemical history of the metal phase. Geochim. Cosmochim. Acta 41, 93–111.

Kobayashi, T., Sueki, K., Ebihara, M., Nakahara, M., Imamura, M., Masuda, A., 1993. Half-lives of technetium-97, technetium-98. Radiochim. Acta 63, 29–31.

Kong, P., Ebihara, M., 1997. The origin and nebular history of the metal phase of ordinary chondrites. Geochim. Cosmochim. Acta 61, 2317–2329.

Lazar, G.C., 2001. Experimental partitioning of Tc, Mo, and Ru in Fe–Ni–S at 60 kb: implications for asteroidal core chemistry. Columbia University, MSc Thesis.

Lugmair, G.W., Galer, S.J.G., 1992. Age and isotopic relationships among the angrites Lewis Cliff 86010 and Angra dos Reis. Geochim. Cosmochim. Acta 56, 1673–1694.

Lugmair, G.W., MacIsaac, C., Shukolyukov, A., 1992. The ^{53}Mn–^{53}Cr isotope system and early planetary evolution. Lunar and Planetary Science Conference, Lunar and Planetary Institute, Houston, pp. 823–824.

Mason, B., Taylor, S.R., 1982. Inclusions in the Allende Meteorite. Smithson. Contrib. Earth Sci. 25, 1–30.

Merrill, P.W., 1952. Spectroscopic observations of stars of class-S. Astrophys. J. 116, 21–26.

Meyer, B.S., 1994. The r-, s-, and p-processes in nucleosynthesis. Annu. Rev. Astron. Astrophys. 32, 153–190.

Morgan, J., Lovering, J., 1967. Rhenium and osmium abundances in chondritic meteorites. Geochim. Cosmochim. Acta 31, 1893–1909.

Morgan, J.W., Walker, R.J., 1989. Isotopic determinations of rhenium and osmium in meteorites by using fusion, distillation and ion-exchange separations. Anal. Chim. Acta 222, 291–300.

Morgan, J.W., Higuchi, H., Takahashi, H., Hertogens, J., 1978. A "chondritic" eucrite parent body: inference from trace elements. Geochim. Cosmochim. Acta 42, 27–38.

Nier, A.O., 1950. A redetermination of the relative abundances of the isotopes of carbon, nitrogen, oxygen, argon and potassium. Phys. Rev. 77, 789–793.

Nyquist, L.E., Bansal, B., Wiesmann, H., Shih, C.-Y., 1994. Neodymium, strontium, and chromium isotopic studies of the LEW86010 and Angra dos Reis meteorites and the chronology of the angrite parent body. Meteoritics 29, 872–885.

O'Neill, H.S.C., Dingwell, D.B., Borisov, A., Spettel, B., Palme, H., 1995. Experimental petrochemistry of some highly siderophile elements at high temperatures, and some implications for core formation and the mantle's early history. Chem. Geol. 120, 255–273.

Palme, H., Wlotzka, F., 1976. A metal particle from a Ca, Al-rich inclusion from the meteorite Allende, and the condensation of refractory siderophile elements. Earth Planet. Sci. Lett. 33, 45–60.

Palme, H., Hutcheon, I.D., Spettel, B., 1994. Composition and origin of refractory-metal-rich assemblages in a Ca, Al-rich Allende inclusion. Geochim. Cosmochim. Acta 58, 495–513.

Pernicka, E., Wasson, J.T., 1987. Ru, Re, Os, Pt and Au in iron meteorites. Geochim. Cosmochim. Acta 51, 1717–1726.

Poths, H., Schmitt-Strecker, S., Begemann, F., 1987. On the isotopic composition of ruthenium in the Allende and Leoville carbonaceous chondrites. Geochim. Cosmochim. Acta 51, 1143–1149.

Qi-Lu, Masuda, A., 1994. The isotopic composition and atomic weight of molybdenum. Int. J. Mass Spectrom. Ion Process. 130, 65–72.

Rayet, M., Arnould, M., Hashimoto, M., Prantzos, N., Nomoto, K., 1995. The p-process in Type II supernovae. Astron. Astrophys. 298, 517–527.

Rayet, M., Costa, V., Arnould, M., 2001. News from the p-process: is the s-process a troublemaker? Nucl. Phys., A 688, 74C–81C.

Righter, K., Drake, M.J., 1997. Metal–silicate equilibrium in a homogeneously accreting Earth: new results for Re. Earth Planet. Sci. Lett. 146, 541–553.

Russell, W.A., Papanastassiou, D.A., Tombrello, T.A., 1978. Ca isotope fractionation on the Earth and other solar system materials. Geochim. Cosmochim. Acta 42, 1075–1090.

Schatz, G., 1983. Note on technetium in stars. Astron. Astrophys. 122, 327–329.

Schönbächler, M., Rehkämper, M., Halliday, A.N., Lee, D.-C., Bourot-Denise, M., Zanda, B., Hattendorf, B., Günther, D., 2002. Niobium–zirconium chronometry and early solar system development. Science 295, 1705–1708.

Smith, V.V., Lambert, D.L., 1988. s-Process-enriched cool stars with and without technetium: clues to asymptotic giant branch and binary star evolution. Astrophys. J. 333, 219–226.

Smoliar, M.I., 1998. Ru isotopic anomalies in iron meteorites: outlook for the Tc–Ru–Mo chronometers. Lunar and Planetary Science, vol. XXIX. Lunar and Planetary Institute, Houston. (CD-ROM), pp. Abstract #1202.

Sylvester, P.J., Ward, B.J., Grossman, L., Hutcheon, I.D., 1990. Chemical compositions of siderophile element-rich opaque assemblages in an Allende inclusion. Geochim. Cosmochim. Acta 54, 3491–3508.

Vance, D., Thirlwall, M., 2002. An assessment of mass discrimination in MC-ICPMS using Nd isotopes. Chem. Geol. 185, 227–240.

Walker, R.J., Horan, M.F., Morgan, J.W., Becker, H., Grossman, J.N., 2002. Comparative 187Re–187Os systematics of chondrites: implications regarding early solar system processes. Geochim. Cosmochim. Acta 66, 4187–4201.

Wasserburg, G.J., 1985. Short-lived nuclei in the early solar system. In: Black, D.C., Matthews, M.S. (Eds.), Protostars and Planets II. University of Arizona Press, Tucson, pp. 703–773.

Wasserburg, G.J., Busso, M., Gallino, R., Raiteri, C.M., 1994. Asymptotic giant branch stars as a source of short-lived radioactive nuclei in the solar nebula. Astrophys. J. 424, 412–428.

Wasserburg, G.J., Busso, M., Gallino, R., 1996. Abundances of actinides and short-lived nonactinides in the interstellar medium: diverse supernova sources for the r-process. Astrophys. J. 466, L109–L113.

Wasson, J.T., Kallemeyn, G.W., 1988. Composition of chondrites. Philos. Trans. R. Soc. Ser. A 325, 535–544.

Weast, R.C., Astle, M.J. (Eds.), 1990. Handbook of Chemistry and Physics. CRC Press, Boca Raton, FL.

Yin, Q., 1995. N-TIMS technique for the Re–Os and Ru isotope systems and its application to selected geochemical and cosmochemical problems. PhD thesis, University of Mainz.

Yin, Q.Z., Jacobsen, S.B., McDonough, W.F., Horn, I., 2000. Supernova sources and the ^{92}Nb–^{92}Zr p-process chronometer. Astrophys. J. 536, L49–L53.